Reality of linear and angular momentum expectation values in bound states

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ABSTRACT

In quantum mechanics textbooks the momentum operator is defined in the Cartesian coordinates and rarely the form of the momentum operator in spherical polar coordinates is discussed. Consequently one always generalizes the Cartesian prescription to other coordinates and falls in a trap. In this work we introduce the difficulties one faces when the question of the momentum operator in spherical polar coordinate comes. We have tried to point out most of the elementary quantum mechanical results, related to the momentum operator, which has coordinate dependence. We explicitly calculate the momentum expectation values in various bound states and show that the expectation value really turns out to be zero, a consequence of the fact that the momentum expectation value is real. We comment briefly on the status of the angular variables in quantum mechanics and the problems related in interpreting them as dynamical variables. At the end, we calculate the Heisenberg's equation of motion for the radial component of the momentum for the Hydrogen atom.

I. INTRODUCTION

Quantum mechanics is a treasure house of peculiar and interesting things. Elementary textbooks of quantum mechanics [1, 2, 3] generally start with the postulates which are required to define the nature of the dynamical variables in the theory and their commutation relations. The choice of the dynamical variables is not that clear, as the coordinates in Cartesian system are all elevated to the status of operators where as time remains a parameter. More over in spherical polar coordinates only the radial component can be represented as an operator while the angles still remain as a problem. The difficulty of giving different status to the spatial coordinates and time is bypassed in quantum field theories where all the coordinates and time become parameters of the theory. But the problem with angles still remain a puzzle which requires to be understood in future.

When we start to learn quantum mechanics, most of the time we begin with elementary calculations relating to the particle in a one dimensional infinite well, particle in a finite potential well, linear harmonic oscillator and so on. The main aim of these calculations is to solve the Schrödinger equation in the specific cases and find out the bound state energies and the energy eigenfunctions in coordinate space representation. While solving these problems we overlook the subtleties of other quantum mechanical objects as the definition of the momentum operator in various coordinates, the reality of its expectation value, etc.. In the last one or two decades there has been a number of studies regarding the self-adjointness of various operators [4]. The aim of these studies has been to analyze the self-adjointness of various operators like momentum, Hamiltonian etc. and find out whether these operators are really self-adjoint in some interval of space where the theory is defined, if not then can there be any mathematical method by which we can make these operators to be self-adjoint in the specified intervals ?

In the present work we deal with a much elementary concept in quantum mechanics related to the reality of the expectation values of the momentum operator, be it linear or angular. We do not analyze the self-adjointness of the operators which requires different mathematical techniques. To test the self-adjointness of an operator we have to see whether the operator is symmetric in a specific spatial interval and the functional domain of the operator and its adjoint are the same. In the article we always keep in touch with the recent findings from modern research about self-adjoint extensions but loosely we assume that the operators which we are dealing with are Hermitian. If something is in contrary we point it out in the main text. A considerable portion of our article deals with the analysis

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of the fact that the expectation value of the momentum operator in various bound states are zero, a result which most of the textbooks only quote but never show. In the simpler cases the result can be shown by one or two lines of calculation, but in nontrivial potentials as the Morse potential, the Coulomb potential the result is established by using various properties of the special functions such as the associated Legendre and the associated Laguerre.

The presentation of various materials in our article is done in the following way. Next section deals with the definition of the momentum operator and its properties. Section III deals with the intricacies of the definition of the momentum operator in spherical polar coordinates and the problems we face when we try to mechanically implement the quantization condition, which is invariably always written in Cartesian coordinates in most of the textbooks on quantum mechanics. In section IV we explicitly calculate the momentum expectation values in various potentials and show that in bound states we always get the expectation value of the linear momentum to be zero. Section V gives a brief discussion on the Ehrenfest theorem when we are using it to find out the time derivative of the expectation value of the radial component of momentum in the case of the Hydrogen atom. We end with the concluding section which summarizes the findings in our article.

Before going into the main discussion we would like to mention about the convention. We have deliberately put a hat over various symbols to show that they are operators in quantum mechanics. Some times this convention becomes tricky when we are dealing with angular variables as there the status of these variables is in question. The other symbols have their conventional meaning. As we are always using the coordinate representation sometimes we may omit the hat over the position operator as in this representation the position operator and its eigenvalues can be trivially interchanged.

II. DEFINITION OF THE MOMENTUM OPERATOR AND THE REALITY OF ITS EXPECTATION VALUE

From the Poisson bracket formalism of classical mechanics we can infer:

$$[\hat{x}_i, \hat{p}_j] = i\hbar\, \delta_{i\,j}\,, \tag{2.1}$$

where $\delta_{i\,j} = 1$ when $i = j$ and zero for all other cases, and $i, j = 1, 2, 3$. In the above equation $\hat{x}_i$ is the position operator and $\hat{p}_j$ is the linear momentum operator in Cartesian coordinates. From the above equation we can also find the form of the momentum operator in position representation, which is:

$$\hat{p}_i = -i\hbar \frac{\partial}{\partial x_i}\,. \tag{2.2}$$

It is interesting to note that the above expression of the momentum operator also gives us the form of the generator of translations. This is because of the property:

$$[\hat{p}_x, F(\hat{x})] = -i\hbar \frac{dF(\hat{x})}{dx}\,, \tag{2.3}$$

where $F(\hat{x})$ is an arbitrary well defined function of $\hat{x}$. The above equation ensures that the momentum operator generates translations along the x direction.

Particularly in one-dimension the expression of the momentum operator becomes $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$. We know that the expectation value of the momentum operator must be real. If we focus on one-dimensional systems to start with, where the system is specified by the wave-function $\psi(x,t)$, the expectation value of any operator $\hat{O}$ is defined by:

$$\langle \hat{O} \rangle \equiv \int_{-\infty}^{\infty} \psi^*(x,t)\, \hat{O}\, \psi(x,t)\, dx\,, \tag{2.4}$$

where ψ^* signifies complex conjugation of ψ and the extent of the system is taken as $-\infty < x < \infty$. From the above equation we can write,

$$\langle \hat{O} \rangle^* = \int_{-\infty}^{\infty} \psi(x,t)\, \hat{O}^*\, \psi(x,t)^*\, dx\,. \tag{2.5}$$

If $\langle \hat{O} \rangle = \langle \hat{O} \rangle^*$ then the condition of the reality of the expectation value becomes:

$$\int_{-\infty}^{\infty} \psi^*(x,t)\, \hat{O}\, \psi(x,t)\, dx = \int_{-\infty}^{\infty} \psi(x,t)\, \hat{O}^*\, \psi(x,t)^*\, dx\,. \tag{2.6}$$

For a three-dimensional system the above condition becomes,

$$\int_{-\infty}^{\infty} \psi^*(\mathbf{x},t)\,\hat{O}\,\psi(\mathbf{x},t)\,d^3x = \int_{-\infty}^{\infty} \psi(\mathbf{x},t)\,\hat{O}^*\,\psi(\mathbf{x},t)^*\,d^3x\,. \tag{2.7}$$

Now if we take the specific case of the momentum operator in one-dimension we can explicitly show that its expectation value is real if the extent of the system is infinite and the wave-function vanishes at infinity. The proof is as follows. The expectation value of the momentum operator is:

$$\begin{aligned}\int_{-\infty}^{\infty} \psi^*(x,t)\,\hat{p}_x\,\psi(x,t)\,dx &= -i\hbar\int_{-\infty}^{\infty}\psi^*(x,t)\,\frac{\partial\psi(x,t)}{\partial x}\,dx \\ &= -i\hbar\left[\psi^*(x,t)\psi(x,t)|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\psi(x,t)\frac{\partial\psi(x,t)^*}{\partial x}\,dx\right],\end{aligned} \tag{2.8}$$

If the wave functions vanish at infinity then the first term on the second line on the right-hand side of the above equation drops and we have,

$$\begin{aligned}\int_{-\infty}^{\infty} \psi^*(x,t)\,\hat{p}_x\,\psi(x,t)\,dx &= -i\hbar\int_{-\infty}^{\infty}\psi^*(x,t)\,\frac{\partial\psi(x,t)}{\partial x}\,dx \\ &= i\hbar\int_{-\infty}^{\infty}\psi(x,t)\frac{\partial\psi(x,t)^*}{\partial x}\,dx\,, \\ &= \int_{-\infty}^{\infty}\psi(x,t)\,\hat{p}_x^*\,\psi(x,t)^*\,dx\,.\end{aligned} \tag{2.9}$$

A similar proof holds for the three-dimensional case where it is assumed that the wave-function vanishes at the boundary surface at infinity.

III. THE EXPECTATION VALUE OF THE MOMENTUM OPERATOR IN CARTESIAN AND SPHERICAL POLAR COORDINATES

In non-relativistic version of quantum mechanics we know that if we have a particle of mass m which is present in a time-independent potential we can separate the Schrödinger equation:

$$i\hbar\frac{\partial\psi(\mathbf{x},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x})\right]\psi(\mathbf{x},t)\,, \tag{3.1}$$

into two equations, one is the time-dependent one which gives the trivial solution $e^{-\frac{iEt}{\hbar}}$ where E is the total energy of the particle, and the other equation is the time-independent Schrödinger equation:

$$\nabla^2 u(\mathbf{x}) + \frac{2m}{\hbar^2}(E - V(\mathbf{x}))u(\mathbf{x}) = 0\,, \tag{3.2}$$

where $u(\mathbf{x})$ is the solution of the time-independent Schrödinger equation and the complete solution of the Eq. (3.1) is:

$$\psi(\mathbf{x},t) = u(\mathbf{x})e^{-\frac{iEt}{\hbar}}\,. \tag{3.3}$$

In the case of the free-particle, where $V(\mathbf{x}) = 0$, we have $u(\mathbf{x},t) = e^{i\mathbf{k}\cdot\mathbf{x}}$ where $E = \frac{k^2\hbar^2}{2m}$ and $k = |\mathbf{k}|$. The free-particle solution is an eigenfunction of the momentum operator with eigen value $\hbar k$. Although if we try to find out the expectation value of the momentum operator as is done in the last section we will be in trouble as these wave-functions do not vanish at infinity, a typical property of free-particle solutions. But this problem is not related to the Hermiticity property of the momentum operator, it is related with the de-localized nature of the free-particle solution.

In physics many times we require to solve a problem using curvilinear coordinate systems. The choice of our coordinate system depends upon the specific symmetry which we have at hand. Suppose we are working in spherical polar coordinates and the solution of Eq. (3.2) can be separated into well behaved functions of r, θ and ϕ as,

$$u(\mathbf{x}) = u(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)\,. \tag{3.4}$$

If we try to follow the proof of the Hermiticity of the linear momenta components, as done in the last section, in spherical polar coordinates, then we should write:

$$\begin{aligned}\langle\hat{\mathbf{p}}\rangle &= -i\hbar\int_\tau u^*(r,\theta,\phi)\nabla u(r,\theta,\phi)\,d\tau\,,\\ &= -i\hbar\int R^*(r)\Theta^*(\theta)\Phi^*(\phi)\,\left[\mathbf{e}_r\frac{\partial}{\partial r}+\frac{\mathbf{e}_\theta}{r}\frac{\partial}{\partial\theta}+\frac{\mathbf{e}_\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right]R(r)\Theta(\theta)\Phi(\phi)r^2\,dr d\Omega\,,\end{aligned} \tag{3.5}$$

where in the above equation $\mathbf{e}_r$, $\mathbf{e}_\theta$, $\mathbf{e}_\phi$ respectively are the unit vectors along r, θ and ϕ, and $d\Omega = \sin\theta\,d\theta\,d\phi$. τ is the volume over which we integrate the expression in the above equation. From the last equation we can write:

$$\langle\hat{p}_r\rangle = -i\hbar\left[\int_\Omega|\Theta(\theta)|^2|\Phi(\phi)|^2d\Omega\right]\int_0^\infty r^2R^*(r)\frac{dR(r)}{dr}\,dr\,, \tag{3.6}$$

As $\Theta(\theta)$ and $\Phi(\phi)$ are normalized, the integration: $\int_\Omega|\Theta(\theta)|^2|\Phi(\phi)|^2d\Omega = 1$ and we can proceed as in Eq. (2.9) as:

$$\begin{aligned}\langle\hat{p}_r\rangle &= -i\hbar\int_0^\infty r^2R^*(r)\frac{dR(r)}{dr}\,dr\,,\\ &= -i\hbar\left[r^2R^*(r)R(r)\big|_0^\infty-\int_0^\infty\left(2rR^*(r)+r^2\frac{dR^*(r)}{dr}\right)R(r)\,dr\right]\,.\end{aligned} \tag{3.7}$$

If $R(r)$ vanishes at infinity then the above equation reduces to,

$$\begin{aligned}\langle\hat{p}_r\rangle &= \left[i\hbar\int_0^\infty r^2R(r)\frac{dR^*(r)}{dr}\,dr\right]+2i\hbar\int_0^\infty r|R(r)|^2\,dr\,,\\ &= \langle\hat{p}_r\rangle^*+2i\hbar\int_0^\infty r|R(r)|^2\,dr\,.\end{aligned} \tag{3.8}$$

The above equation implies that $\langle\hat{p}_r\rangle$ is not real in spherical polar coordinates. The solution of the above problem lies in redefining $\hat{p}_r$ as is evident from Eq. (3.8), and it was given by Dirac [5, 6]. The redefined linear momentum operator along r can be:

$$\hat{p}_r \equiv -i\hbar\left(\frac{\partial}{\partial r}+\frac{1}{r}\right) = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}\,r\,. \tag{3.9}$$

This definition of the $\hat{p}_r$ is suitable because in this form it satisfies the commutation relation as given in Eq. (2.1) where now the operator conjugate to $\hat{r}$ is $\hat{p}_r$. The form of $\hat{p}_r$ in Eq. (3.9) shows that for any arbitrary function of r as $F(r)$ we must still have Eq. (2.3) satisfied. This implies that the modified form of $\hat{p}_r$ is still a generator of translations along the r direction. Up to this point we were following what was said by Dirac regarding the status of the radial momentum operator. Still everything is not that smooth with the redefined operator as we can see that it turns out to be singular around $r = 0$, more over, although the radial momentum acts like a translation generator along r but near $r = 0$ it cannot generate a translation towards the left as the interval ends there.

In this regard we can state that the issue of the reality of the radial component of the momentum in spherical polar coordinates is a topic of modern research in theoretical physics [7, 8]. It has been shown that the operator $-i\hbar\frac{\partial}{\partial r}$ is not Hermitian and more over it can be shown [4] that such an operator cannot be self-adjoint in the interval $[0,\infty]$. In some recent work [8] the author claims that there can be an unitary operator which connects $-i\hbar\frac{\partial}{\partial r}$ to $-i\hbar\frac{1}{r}\frac{\partial}{\partial r}\,r$, and as the former operator does not have a self-adjoint extension in the semi-infinite interval so the latter is also not self-adjoint in the same interval.

If we further try to find out whether $\langle\hat{p}_\theta\rangle$ and $\langle\hat{p}_\phi\rangle$ are real, then we will face difficulties. Working out naively if we claim that $\hat{p}_\phi = \frac{1}{rsin\theta}\frac{\partial}{\partial\phi}$ as suggested by the ϕ component of Eq. (3.5) we will notice that $\phi\,\hat{p}_\phi$ does not have the dimension of action. This means $\hat{p}_\phi$ or $\hat{p}_\theta$ is not conjugate to ϕ or θ. This is a direct representation of the special coordinate dependence of the quantization condition. Only in Cartesian coordinates the variables conjugate to x, y and z are p_x, p_y and p_z. Taking the clue from classical mechanics we know the proper dynamical variables conjugate to $\hat{\phi}$ and $\hat{\theta}$ are the angular momentum operators, namely $\hat{L}_\theta$ and $\hat{L}_\phi$. In general $\hat{L}_\phi$ is given by:

$$\hat{L}_\phi = -i\hbar\frac{\partial}{\partial\phi}\,, \tag{3.10}$$

which can be shown to posses real expectation values by following a similar proof as is done in Eq. (2.8) and Eq. (2.9), if we assume $\Phi(0) = \Phi(2\pi)$. In this form it is tempting to say that we can have a relation of the form,

$$[\hat{\phi}, \hat{L}_\phi] = i\hbar\,, \tag{3.11}$$

which looks algebraically correct. But the difficulty in writing such an equation is in the interpretation of $\hat{\phi}$ which has been elevated from an angular variable to a dynamical operator. In spherical polar coordinates both θ and ϕ are compact variables and consequently have their own subtleties. Much work is being done in trying to understand the status of angular variables and phases [9, 10], in this work we only present one example showing the difficulty of accepting $\hat{\phi}$ as an operator.

From the solution of the time-independent Schrödinger equation for an isotropic potential we will always have:

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{iM\phi}\,, \tag{3.12}$$

where $M = 0, \pm1, \pm2, \cdot, \cdot$. Now if $\hat{\phi}$ is an operator we can find its expectation value, and it turns out to be:

$$\begin{aligned} \langle\hat{\phi}\rangle &= \frac{1}{2\pi}\int_0^{2\pi} \phi e^{iM\phi} e^{-iM\phi}\, d\phi\,, \\ &= \pi\,, \end{aligned} \tag{3.13}$$

and the expectation value of $\hat{\phi}^2$ is:

$$\begin{aligned} \langle\hat{\phi}^2\rangle &= \frac{1}{2\pi}\int_0^{2\pi} \phi^2 e^{iM\phi} e^{-iM\phi}\, d\phi\,, \\ &= \frac{4}{3}\pi^2\,. \end{aligned} \tag{3.14}$$

Consequently $\Delta\phi = \sqrt{\langle\hat{\phi}^2\rangle - \langle\hat{\phi}\rangle^2} = \frac{\pi}{\sqrt{3}}$. Similarly calculating $\hat{L}_\phi$ we get:

$$\begin{aligned} \langle\hat{L}_\phi\rangle &= \frac{M\hbar}{2\pi}\int_0^{2\pi} e^{-iM\phi} e^{iM\phi}\, d\phi\,, \\ &= M\hbar\,, \end{aligned} \tag{3.15}$$

as expected, and $\langle\hat{L}_\phi^2\rangle = M^2\hbar^2$. This implies $\Delta L_\phi = \sqrt{\langle\hat{L}_\phi^2\rangle - \langle\hat{L}_\phi\rangle^2} = 0$. So we can immediately see that the Heisenberg uncertainty relation between $\hat{\phi}$ and $\hat{L}_\phi$, $\Delta\phi\Delta L_\phi \geq \hbar/2$ breaks down. This fact makes life difficult and we have no means to eradicate this problem.

Taking the clue from the ϕ part we can propose that $\hat{L}_\theta$ is also of the form $-i\hbar\frac{\partial}{\partial\theta}$. With this definition of $\hat{L}_\theta$ let us try to prove its Hermitian nature as done in Eq. (3.7). Taking $R(r)$ and $\Phi(\phi)$ in Eq. (3.4) separately normalized, we can write:

$$\begin{aligned} \langle\hat{L}_\theta\rangle &= -i\hbar\int_0^{\pi} \Theta^*(\theta)\frac{d\Theta(\theta)}{d\theta}\, \sin\theta d\theta \\ &= -i\hbar\left[\sin\theta\,\Theta^*(\theta)\Theta(\theta)|_0^\pi - \int_0^\pi \left(\cos\theta\,\Theta^*(\theta) + \sin\theta\frac{d\Theta^*(\theta)}{d\theta}\right)\Theta(\theta)\, d\theta\right]\,, \\ &= \left[i\hbar\int_0^\pi \sin\theta\,\Theta(\theta)\frac{d\Theta^*(\theta)}{d\theta}\, d\theta\right] + i\hbar\int_0^\pi \cos\theta\,|\Theta(\theta)|^2\, d\theta\,, \\ &= \langle\hat{L}_\theta\rangle^* + i\hbar\int_0^\pi \cos\theta\,|\Theta(\theta)|^2\, d\theta\,. \end{aligned} \tag{3.16}$$

The above equation shows that $\langle\hat{L}_\theta\rangle$ is not real. The rest is similar to the analysis following Eq. (3.8) where now we have to redefine the angular momentum operator conjugate to θ as [11]:

$$\hat{L}_\theta \equiv -i\hbar\left(\frac{\partial}{\partial\theta} + \frac{1}{2}\cot\theta\right)\,. \tag{3.17}$$

Unlike the ϕ case, $\Theta(\theta)$ are not eigenfunctions of $\hat{L}_\theta$. But the difficulties of establishing θ as an operator still persists and in general θ is not taken to be a dynamical operator in quantum mechanics.

It is known that both θ and ϕ are compact variables, i.e. they have a finite extent. But there is a difference between them. In spherical polar coordinates the range of ϕ and θ are not the same, $0 \leq \phi < 2\pi$ and $0 \leq \theta \leq \pi$. This difference can have physical effects. As ϕ runs over the whole angular range so the wave-function corresponding to it $\Phi(\phi)$ is periodic in nature while due to the range of θ, $\Theta(\theta)$ need not be periodic. Consequently there can be a net angular momentum along the ϕ direction while there cannot be any net angular momentum along θ direction. And this can be easily shown to be true. As the time-independent Schrödinger equation for an isotropic potential yields $\Phi(\phi)$ as given in Eq. (3.12) similarly it is known that in such a potential the form of $\Theta(\theta)$ is given by:

$$\Theta(\theta) = N_\theta \, P_M^L(\cos\theta)\,, \tag{3.18}$$

where N_θ is a normalization constant depending on L, M and $P_M^L(\cos\theta)$ is the associated Legendre function, which is real. In the above equation L and M are integers where $L = 0, 1, 2, 3, \cdot, \cdot$ and $M = 0, \pm 1, \pm 2, \pm 3, \cdot, \cdot$. The quantum number M appearing in Eq. (3.12) and in Eq. (3.18) are the same. This becomes evident when we solve the time-independent Schrödinger equation in spherical polar coordinates by the method of separation of variables. A requirement of the solution is $-L \leq M \leq L$. Now we can calculate the expectation value of $\hat{L}_\theta$ using the above wave-function and it is:

$$\begin{aligned}
\langle \hat{L}_\theta \rangle &= -i\hbar N_\theta^2 \int_0^\pi P_M^L(\cos\theta) \left(\frac{dP_M^L(\cos\theta)}{d\theta} + \frac{1}{2}\cot\theta P_M^L(\cos\theta) \right) \sin\theta d\theta \\
&= -i\hbar N_\theta^2 \left[\int_0^\pi P_M^L(\cos\theta) \frac{dP_M^L(\cos\theta)}{d\theta} \sin\theta d\theta + \frac{1}{2}\int_0^\pi P_M^L(\cos\theta) P_M^L(\cos\theta)\cos\theta \, d\theta \right] .
\end{aligned} \tag{3.19}$$

To evaluate the integrals on the right hand side of the above equation we can take $x = \cos\theta$ and then the expectation value becomes:

$$\begin{aligned}
\langle \hat{L}_\theta \rangle &= -i\hbar N_\theta^2 \left[\int_1^{-1} P_M^L(x) \frac{dP_L^M(x)}{dx} (1-x^2)^{\frac{1}{2}} \, dx \right. \\
&- \left. \frac{1}{2}\int_1^{-1} P_{M(x)}^L P_{M(x)}^L \frac{x}{\sqrt{1-x^2}} dx \right] .
\end{aligned} \tag{3.20}$$

The second term in the right hand side of the above equation vanishes as the integrand is an odd function in the integration range. For the first integral we use the following recurrence relation [12]:

$$(x^2-1)\frac{dP_M^L(x)}{dx} = MxP_M^L(x) - (L+M)P_{M-1}^L(x)\,, \tag{3.21}$$

the last integral can be written as,

$$\begin{aligned}
\langle \hat{L}_\theta \rangle &= i\hbar N_\theta^2 \left[M \int_1^{-1} x(1-x^2)^{-\frac{1}{2}} P_M^L(x) P_M^L(x) \, dx \right. \\
&- \left. (L+M) \int_1^{-1} (1-x^2)^{-\frac{1}{2}} P_M^L(x) P_{M-1}^L(x) \, dx \right] .
\end{aligned} \tag{3.22}$$

As,

$$P_M^L(x) = (-1)^{L+M} P_M^L(-x)\,, \tag{3.23}$$

we can see immediately that both the integrands in the right hand side of the above equation is odd and consequently $\langle \hat{L}_\theta \rangle = 0$ as expected. A similar analysis gives $\langle \hat{L}_\phi \rangle = M\hbar$. It must be noted that the form of $\hat{L}_\theta$ still permits it to be the generator of rotations along the θ direction.

As the motion along ϕ is closed so there can be a net flow of angular momentum along that direction but because the motion along θ is not so, a net momentum along θ direction will not conserve probability and consequently for probability conservation we must have expectation value of angular momentum along such a direction to be zero. In elementary quantum mechanics text books it is often loosely written that the solution of the time-independent Schrödinger equation is real when we are solving it for a real potential. But this statement is not correct. The reality

of the solution also depends upon the coordinate system used. Specially for compact periodic coordinates we can always have complex functions as solutions without breaking any laws of physics.

Before leaving the discussion on angular variables in spherical polar coordinates we want to point out one simple thing which is interesting. In Cartesian coordinates when we deal with angular momentum we know that:

$$[\hat{L}_i, \hat{L}_j] = i\epsilon_{ijk}\,\hat{L}_k\,, \tag{3.24}$$

where $\hat{L}_i$ stands for $\hat{L}_x$, $\hat{L}_y$ or $\hat{L}_z$. For this reason there cannot be any state which can be labelled by the quantum numbers of any two of the above angular momenta. But from the expressions of $\hat{L}_\phi$ and $\hat{L}_\theta$ we see that,

$$[\hat{L}_\phi, \hat{L}_\theta] = 0\,, \tag{3.25}$$

and consequently in spherical polar coordinates we can have wave-function solutions of the Schrödinger equation which are simultaneous eigenfunctions of both $\hat{L}_\phi$ and $\hat{L}_\theta$ as $P_M^L(\theta)$.

For real $V(\mathbf{x})$, we expect the solution of the time-independent Schrödinger equation $u(\mathbf{x})$ to be real, when we are solving the problem in Cartesian coordinates. In all these cases the expectation value of the linear momentum operators must vanish. The reason is simple and can be understood in one-dimensional cases where with real $u(x)$ we directly see that the integral $\int_{-\infty}^{\infty} u^*(x)\,\frac{\partial u(x)}{\partial x}\,dx$ is real and so $\int_{-\infty}^{\infty} u^*(x)\,\hat{p}_x\,u(x)\,dx$ becomes imaginary as $\hat{p}_x$ contains i, as is evident from the first line in Eq. (2.9). So if the expectation value of the momentum operator has to be real then the only outcome can be that for all those cases where we have a time-independent solution in a bounded region of space, with a real potential and working in Cartesian coordinates, the expectation value of the momentum operator must vanish. The above statement is true in curvilinear coordinates also, but in those cases the definition of the momentum operators have to be modified. This fact becomes clear when we write the relationship between the probability flux and the expectation value of the momentum operator. The probability flux for a particle of mass m is:

$$\begin{aligned}
\mathbf{j}(\mathbf{x},t) &= -\left(\frac{i\hbar}{2m}\right)\left[\psi^*(\mathbf{x},t)\nabla\psi(\mathbf{x},t) - (\nabla\psi^*(\mathbf{x},t))\psi(\mathbf{x},t)\right]\,, \\
&= \left(\frac{\hbar}{m}\right)\mathrm{Im}\left(\psi^*(\mathbf{x},t)\nabla\psi(\mathbf{x},t)\right)\,,
\end{aligned} \tag{3.26}$$

where 'Im' implies the imaginary part of some quantity. Most of the elementary quantum mechanics books then proceeds to show that:

$$\int d^3x\,\mathbf{j}(\mathbf{x},t) = \frac{\langle\hat{\mathbf{p}}\rangle}{m}\,, \tag{3.27}$$

which is obtained from Eq. (3.26) by integrating both sides of it over the whole volume. From Eq. (3.26) we immediately see that if the solution of the time-independent Schrödinger equation is real we will have $\mathbf{j}(\mathbf{x},t) = 0$ and consequently from Eq. (3.27), $\langle\hat{\mathbf{p}}\rangle = 0$. But this statement is also coordinate dependent, which is rarely said in elementary textbooks of quantum mechanics. Eq. (3.26) evidently does not hold in spherical polar coordinates. If we take Eq. (3.4) as the solution in a general isotropic central potential and use the general form of ∇ in spherical polar coordinates then it can be seen that $\mathbf{j}_r(r,\theta,\phi,t) = 0$ for a real potential. But then Eq. (3.27) does not hold as here $\hat{p}_r$ is simply the radial component of ∇ and not as given in Eq. (3.9), and we know $\langle\frac{d}{dr}\rangle$ is not zero. The reason why Eq. (3.26) is not suitable in spherical polar coordinates is related to the fact that in deriving Eq. (3.26) one assumes that the probability density of finding the quantum state within position $\mathbf{x}$ and $\mathbf{x}+d\mathbf{x}$ at time t is $|\psi(\mathbf{x},t)|^2$. But this statement is only true in Cartesian coordinates, in spherical polar coordinates the probability density of the system to be within a region r and $r+dr$, θ and $\theta+d\theta$, ϕ and $\phi+d\phi$ is not $|\psi(r,\theta,\phi)|^2$ but $|\psi(r,\theta,\phi)|^2 r^2\sin\theta$ and consequently the steps which follow leading to Eq. (3.26) in Cartesian coordinates are not valid in spherical polar coordinates. In general Eq. (3.26) will not be valid in any curvilinear coordinate system.

The next section contains the actual calculations of the expectation values of the momentum operator in various cases where we have bound state solutions. In all the relevant cases discussed in this article it is seen that although $\langle\hat{p}_x\rangle = 0$ but $\langle\hat{p}_x^2\rangle$ is not zero as it is related to the Hamiltonian operator. In all the cases we must have,

$$\langle(\hat{p}_x)^s\rangle = 0\,,\ s = \text{odd integer}\,. \tag{3.28}$$

The above equation can be guessed from the reality of the expectation value of the momentum operator.

IV. MOMENTUM EXPECTATION VALUES IN VARIOUS BOUND STATES

In this section we will calculate the momentum expectation values in various bound states with stiff or slowly varying potentials.

A. Particle in one-dimensional stiff potential wells

1. *Infinite square well potential*

In this case we consider a particle to be confined in region $-\frac{L}{2}$ to $\frac{L}{2}$ along the x-axis where the potential is specified by,

$$\begin{aligned} V(\hat{x}) &= \infty\,,\ |x| \geq \frac{L}{2}\,, \\ &= 0\,,\ |x| < \frac{L}{2}\,. \end{aligned} \tag{4.1}$$

In this case the solution of the time-independent Schrödinger equation, Eq. (3.2), satisfies the boundary condition,

$$u\left(-\frac{L}{2}\right) = u\left(\frac{L}{2}\right) = 0\,, \tag{4.2}$$

and as the potential has parity symmetry about $x = 0$ we have two sets of solutions, the odd solutions:

$$u_n^{(o)}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2n\pi x}{L}\right)\,, \tag{4.3}$$

and the even solutions:

$$u_n^{(e)}(x) = \sqrt{\frac{2}{L}} \cos\left(\frac{(2n-1)\pi x}{L}\right)\,. \tag{4.4}$$

In the above equations n is a positive integer. Both of these functions, $u_n^{(o)}(x)$ for the odd case and $u_n^{(e)}(x)$ for the even case, are real and are not momentum eigenstates. But the momentum expectation values can be found out from the above solutions. For the odd solutions we have:

$$\begin{aligned} \langle \hat{p}_x \rangle &= -i\hbar \int_{-\frac{L}{2}}^{\frac{L}{2}} u_n^{(o)}(x) \frac{du_n^{(o)}(x)}{dx}\, dx\,, \\ &= -\frac{4in\pi\hbar}{L^2} \int_{-\frac{L}{2}}^{\frac{L}{2}} \sin\left(\frac{2n\pi x}{L}\right) \cos\left(\frac{2n\pi x}{L}\right)\,, \\ &= 0\,, \end{aligned} \tag{4.5}$$

as expected. Similarly for the even solutions it is also easy to show that the expectation value of the momentum operator vanishes.

2. *Finite square well potential*

In this case,

$$\begin{aligned} V(\hat{x}) &= 0\,,\ |x| \geq a\,, \\ &= -V_0\,, |x| < a\,,\ (V_0 > 0)\,. \end{aligned} \tag{4.6}$$

If we are not interested in the normalization constant of the bound state solution then the solution of the time-independent Schrödinger equation in this case is:

$$\begin{aligned} u(x) &\sim e^{-\kappa|x|}\,,\ |x| > a\,, \\ &\sim \cos(kx)\,,\ |x| < a\,,\ \text{(even parity)} \\ &\sim \sin(kx)\,,\ |x| < a\,,\ \text{(odd parity)}\,, \end{aligned} \tag{4.7}$$

where,

$$k^2 = \frac{2m(-|E|+V_0)}{\hbar^2}\,, \tag{4.8}$$

$$\kappa^2 = \frac{2m|E|}{\hbar^2}\,. \tag{4.9}$$

In this case the expectation value of the momentum operator is:

$$\begin{aligned}\langle\hat{p}_x\rangle &\sim -i\hbar\int_{-\infty}^{+\infty} u(x)\frac{du(x)}{dx}\,dx\,,\\ &\sim -i\hbar\left[\kappa\left(\int_{-\infty}^{-a} e^{2\kappa x}dx - \int_{a}^{\infty} e^{-2\kappa x}dx\right) + k\int_{-a}^{a}\sin(kx)\cos(kx)\,dx\right]\,,\\ &= 0\,,\end{aligned} \tag{4.10}$$

where the first two lines of the above equation holds up to a constant arising from the normalization of the wave-function. In deriving the last equation we have taken the odd parity solution, but the result remains unaffected if we take the even parity solution as well.

3. Dirac-delta potential

In this case the potential is:

$$V(\hat{x}) = -V_0\,\delta(\hat{x})\,,\ (V_0>0)\,. \tag{4.11}$$

In this case there can be one bound state solution which is obtained after solving the Eq. (3.2). Demanding that the solution $u(x)$ satisfies the boundary conditions:

$$u(x=-\epsilon) = u(x=+\epsilon)\,, \tag{4.12}$$

$$\left.\frac{du}{dx}\right|_{x=+\epsilon} - \left.\frac{du}{dx}\right|_{x=-\epsilon} = -\frac{2mV_0}{\hbar^2}\,u(x=0)\,, \tag{4.13}$$

where ϵ is an infinitesimal quantity tending to zero, we get the form of the solution which is:

$$u(x) = \sqrt{\kappa}\,e^{\kappa x}\,,\ x\le 0\,, \tag{4.14}$$

$$= \sqrt{\kappa}\,e^{\kappa x}\,,\ x\ge 0\,, \tag{4.15}$$

where $\kappa = \frac{mV_0}{\hbar^2}$ and the energy of the bound state is $E = -\frac{mV_0^2}{2\hbar^2}$.

The expectation value of the momentum operator in this case is:

$$\begin{aligned}\langle\hat{p}_x\rangle &= -i\hbar\int_{-\infty}^{\infty} u(x)\frac{du(x)}{dx}\,dx\,,\\ &= -i\hbar\kappa\left[\int_{-\infty}^{0} e^{2\kappa x}\,dx - \int_{0}^{\infty} e^{-2\kappa x}\,dx\right]\,,\\ &= 0\,.\end{aligned} \tag{4.16}$$

In this case, also from Hermiticity of the momentum operator we see that Eq. (3.28) holds true.

B. Particle in one-dimensional slowly varying potentials

1. Linear harmonic oscillator potential

In the case of the linear harmonic oscillator we have:

$$V(\hat{x}) = \frac{1}{2}m\omega^2\hat{x}^2\,, \tag{4.17}$$

where ω is the angular frequency of the oscillator. The solution of Eq. (3.2) in this case, using the series solution method, yields:

$$u_n(q) = N_n\, e^{-\frac{q^2}{2}} H_n(q)\,, \tag{4.18}$$

where $n = 0, 1, 2, \cdot, \cdot$ and $q = \sqrt{\alpha}x$ where $\alpha = \frac{m\omega}{\hbar^2}$. $H_n(q)$ are Hermite polynomials of order n and N_n is the normalization constant given by,

$$N_n = \left(\frac{1}{\sqrt{\pi}\, n!\, 2^n}\right)^{\frac{1}{2}}\,. \tag{4.19}$$

The momentum expectation value in this case turns out to be,

$$\begin{aligned}
\langle \hat{p}_x \rangle &= -i\hbar\sqrt{\alpha}\int_{-\infty}^{\infty} u_n(q)\frac{du_n(q)}{dq}\,dq\,,\\
&= -i\hbar\sqrt{\alpha}N_n^2\left[\int_{-\infty}^{\infty} e^{-q^2} H_n(q)\frac{dH_n(q)}{dq}\,dq - \int_{-\infty}^{\infty} q\, e^{-q^2} H_n^2(q)\,dq\right]\,,\\
&= 0\,.
\end{aligned} \tag{4.20}$$

The first integral on the right side of the second line of the last equation vanishes because, $\frac{dH_n(q)}{dq} = 2nH_{n-1}(q)$ and consequently the integral transforms into the orthogonality condition of the Hermite polynomials. The second integral on the second line of the right side of the above equation vanishes because the integrand is an odd function of q.

The linear harmonic oscillator (LHO) has some very interesting properties. To unravel them we have to digress a bit from the wave-mechanics approach which we have been following and follow the Dirac notation of *bra* and *kets*. The Hamiltonian of the LHO in one-dimension is:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\,, \tag{4.21}$$

which can also be written as:

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\,, \tag{4.22}$$

where $\hat{a}$ and $\hat{a}^\dagger$ are the annihilation and the creation operators given by:

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}_x}{m\omega}\right)\,,\ \hat{a}^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}_x}{m\omega}\right)\,. \tag{4.23}$$

It can be seen clearly from the above definitions that $\hat{a}$ is not an Hermitian operator. More over from the definition of the operators we see that,

$$[\hat{a}, \hat{a}^\dagger] = 1\,. \tag{4.24}$$

Conventionally the number operator is defined as:

$$\hat{N} \equiv \hat{a}^\dagger\hat{a}\,, \tag{4.25}$$

and its eigen-basis are the number states $|n\rangle$ such that,

$$\hat{N}\,|n\rangle = n|n\rangle\,. \tag{4.26}$$

The Hamiltonian of the LHO can be written in terms of the number operator and consequently the number states are energy eigenstates. In this basis the action of the annihilation and creation operators are as:

$$\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle\,, \tag{4.27}$$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle\,. \tag{4.28}$$

From the definitions of the annihilation and creation operators we can write the momentum operator as:

$$\hat{p}_x = -i\sqrt{\frac{m\hbar\omega}{2}}(\hat{a} - \hat{a}^\dagger)\,. \tag{4.29}$$

From Eq. (4.27), Eq. (4.28) and the above equation we can write the matrix elements of the momentum operator as:

$$\langle n'|\hat{p}_x|n\rangle = i\sqrt{\frac{m\hbar\omega}{2}}\left(-\sqrt{n}\,\delta_{n',\,n-1} + \sqrt{n+1}\,\delta_{n',\,n+1}\right) . \tag{4.30}$$

The above equation shows that the momentum operator can connect two different energy eigenstates.

In the case of LHO, except the number operator states, we can have another state which is an eigenstate of the annihilation operator $\hat{a}$. This state is conventionally called the coherent state and it is given as:

$$|\alpha\rangle = e^{-\frac{|\alpha|^2}{2}}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle\,, \tag{4.31}$$

where α is an arbitrary complex number. Now from Eq. (4.29) we can find the momentum expectation value of the coherent state and it is,

$$\langle\hat{p}_x\rangle_\alpha \equiv \langle\alpha|\hat{p}_x|\alpha\rangle = \sqrt{\frac{m\hbar\omega}{2}}\;\mathrm{Im}(\alpha)\,. \tag{4.32}$$

From the above equation we can see that although the expectation value of the momentum operator is zero in the energy eigen-basis but it is not so when we compute the momentum expectation value in the coherent state basis, which is essentially a superposition of energy eigenstates. It must be noted that the momentum expectation value is non zero only when the parameter α has an imaginary part.

2. Pöschl-Teller potential

Among the potentials belonging to the hypergeometric class the Pöschl-Teller potentials have been the most extensively studied and used. This class of potentials consist of trigonometric as well as the hyperbolic type. The trigonometric versions have found applications in molecular and solid state physics and the hyperbolic variants have been used in various studies related to black hole perturbations.

In the present work we use the trigonometric, symmetric Pöschl-Teller potential given by:

$$V(\hat{x}) = V_0\tan^2(a\hat{x})\,, \tag{4.33}$$

where V_0 can be parameterized as:

$$V_0 = \frac{\hbar^2a^2}{2m}\lambda(\lambda-1)\,, \tag{4.34}$$

with for some positive number $\lambda > 1$ and a is some scaling factor. The energy eigenvalues of the bound state solutions are:

$$E_n = -\frac{\hbar^2a^2}{2m}(n^2+2n\lambda+\lambda)\,, \tag{4.35}$$

and the solution of the time-independent Schrödinger equation is,

$$u_n(x) = N_n\sqrt{\cos(ax)}\,P^{1/2-\lambda}_{n+\lambda-1/2}\left(\sin(ax)\right)\,, \tag{4.36}$$

where,

$$N_n = \left[\frac{a(n+\lambda)\Gamma(n+2\lambda)}{\Gamma(n+1)}\right]^{1/2}\,, \tag{4.37}$$

is the normalization constant and $P^\mu_\nu(x)$ is the associated Legendre function. At this point it is fair to point out that $P^\mu_\nu(x)$ is not the Legendre polynomial $P^L_M(x)$ appearing in Eq. (3.18), as μ and ν need not be integers as L and M. $P^\mu_\nu(x)$ is not a polynomial but the function appearing in the right hand side of Eq. (4.36) is a polynomial.

Now as claimed in the text let us show that the momentum expectation value is indeed zero. Before we proceed let us simplify the notation a bit by calling $\mu = 1/2-\lambda$ and $\nu = n+\lambda-1/2$. Substituting $z = ax$ we can write the momentum expectation value as:

$$\langle\hat{p}_x\rangle = -i\hbar N_n^2\int_{-\pi/2}^{\pi/2}dz\,\sqrt{\cos(z)}\,P^\mu_\nu\left(\sin(z)\right)\frac{d}{dz}\left(\sqrt{\cos(z)}\,P^\mu_\nu\left(\sin(z)\right)\right)\,. \tag{4.38}$$

Note the limits of the integration range from $\pi/2$ to $-\pi/2$ since at this value the potential becomes infinity hence we need not consider the integration range to be the whole real line. For the sake of convenience let us make a change of variable; letting $y = \sin(z)$ the above integral becomes:

$$\langle \hat{p}_x \rangle = -i\hbar N_n^2 \int_{-1}^{+1} dy\, (1-y^2)^{1/4} P_\nu^\mu(y) \frac{d}{dy}\left[(1-y^2)^{1/4} P_\nu^\mu(y)\right] . \tag{4.39}$$

Taking the derivative inside the integral we get:

$$\langle \hat{p}_x \rangle = -i\hbar N_n^2 \int_{-1}^{+1} dy \left[(1-y^2)^{1/2} P_\nu^\mu(y) \frac{dP_\nu^\mu(y)}{dy} - \frac{y(1-y^2)^{-1/2}}{2} P_\nu^\mu(y) P_\nu^\mu(y)\right] . \tag{4.40}$$

It is known that for associated Legendre functions [13],

$$P_\nu^\mu(-x) = \cos[(\mu+\nu)\pi]\, P_\nu^\mu(x) - \frac{2}{\pi} \sin[(\mu+\nu)\pi]\, Q_\nu^\mu(x)\,, \tag{4.41}$$

where $Q_\nu^\mu(x)$ is the other linearly independent solution of the associated Legendre differential equation. As in our case $\mu+\nu = n$ so $P_\nu^\mu(x)$ will have definite parity. As $P_\nu^\mu(x)$ has definite parity so the contribution of the second term in the above integral vanishes since the total integrand is an odd function. The first integral is similar to the one in Eq. (3.20) and, due to the typical parity property of $P_\nu^\mu(x)$ as shown in Eq. (4.41), it also vanishes. Consequently we have $\langle \hat{p}_x \rangle = 0$ as expected.

3. Morse potential

Diatomic molecule is an exactly solvable system, if one neglects the molecular rotation. The most convenient model to describe the system, is the Morse potential [14]:

$$V(\hat{x}) = D(e^{-2\beta\hat{x}} - 2e^{-\beta\hat{x}})\,, \tag{4.42}$$

where $x = r/r_0 - 1$, which is the distance from the equilibrium position scaled by the equilibrium value of the inter-nuclear distance r_0. D is the depth of the potential, called dissociation energy of the molecule and β being a parameter which controls the width of the potential.

In terms of the above scaled variable x, the time-independent Schrödinger equation becomes:

$$-\frac{\hbar^2}{2\mu r_0}\frac{d^2u(x)}{dx^2} + D(e^{-2\beta x} - 2e^{-\beta x})u(x) = Eu(x)\,. \tag{4.43}$$

Here μ is the reduced mass of the molecule and the corresponding bound state eigen function comes out to be:

$$u_n^\lambda(\xi) = Ne^{-\xi/2}\xi^{s/2} L_n^s(\xi)\,, \tag{4.44}$$

where the variables are described as,

$$\xi = 2\lambda e^{-y};\;\; y = \beta x;\;\; 0 < \xi < \infty\,, \tag{4.45}$$

and

$$n = 0, 1, ..., [\lambda - 1/2]\,, \tag{4.46}$$

which is nothing but the quantum number of the vibrational bound states. Here $[\rho]$ denotes the largest integer smaller than ρ, thus total number of bound states is $[\lambda - 1/2] + 1$. The parameters,

$$\lambda = \sqrt{\frac{2\mu D r_0^2}{\beta^2\hbar^2}} \;\text{ and }\; s = \sqrt{-\frac{8\mu r_0^2}{\beta^2\hbar^2}E}\,, \tag{4.47}$$

satisfy the constraint condition $s + 2n = 2\lambda - 1$. We note that the parameter λ is potential dependent and s is related to energy E. In Eq. (4.44), $L_n^s(y)$ is the associated Laguerre polynomial and N is the normalization constant [15]:

$$N = \left[\frac{\beta(2\lambda - 2n - 1)\Gamma(n+1)}{\Gamma(2\lambda - n)r_0}\right]^{1/2} . \tag{4.48}$$

We are looking for the expectation value of linear momentum for a vibrating diatomic molecule, and its expression is:

$$\langle \hat{p}_x \rangle = -i\hbar \int_{-\infty}^{\infty} u_n^*(\xi) \frac{d}{dx} u_n(\xi) dx \,. \tag{4.49}$$

In terms of the changed variable $\xi = 2\lambda e^{-\beta x}$ the integration limit changes to ∞ to 0 and the expectation value becomes:

$$\begin{aligned} \langle \hat{p}_x \rangle &= -i\hbar \int_{\infty}^{0} u_n^*(\xi) \frac{d}{d\xi} u_n(\xi) d\xi \\ &= i\hbar N^2 \left[-\frac{1}{2} \int_0^{\infty} e^{-\xi} \xi^s (L_n^s(\xi))^2 d\xi + \frac{s}{2} \int_0^{\infty} e^{-\xi} \xi^{s-1} (L_n^s(\xi))^2 d\xi \right. \\ &+ \left. \int_0^{\infty} e^{-\xi} \xi^s L_n^s(\xi) \frac{d}{d\xi} L_n^s(\xi) d\xi \right] \\ &= i\hbar N^2 \left[-\frac{1}{2} I_1 + \frac{s}{2} I_2 + I_3 \right] . \end{aligned} \tag{4.50}$$

Integral I_1 is the orthogonality relation of the associated Laguerre polynomials, which is:

$$\int_0^{\infty} e^{-\xi} \xi^s L_n^s(\xi) L_m^s(\xi) d\xi = \frac{\Gamma(s+n+1)}{\Gamma(n+1)} \delta_{m,n} \,. \tag{4.51}$$

To evaluate the second integral one uses the normalization integral of Morse eigenstates. The normalization relation is:

$$\int_{-\infty}^{\infty} u^*(\xi) u(\xi) dr = \frac{|N|^2 r_0}{\beta} \int_0^{\infty} e^{-\xi} \xi^{s-1} (L_n^s(\xi))^2 d\xi = 1 \,. \tag{4.52}$$

The above integral involving ξ, is explicitly I_2. N, being the normalization constant as given in Eq. 4.48. Thus it is very straight forward to evaluate I_2 from the above relation as,

$$I_2 = \frac{\Gamma(n+s+1)}{s\,\Gamma(n+1)} \,. \tag{4.53}$$

The last integrand I_3 includes a differentiation which can be written as [16]:

$$\frac{d}{d\xi} L_n^s(\xi) = -L_{n-1}^{s+1}(\xi) \,. \tag{4.54}$$

Writing the right hand side of the above equation as a summation [17]:

$$L_n^{s+1} = \sum_{m=0}^{n} L_m^s \,, \tag{4.55}$$

and substituting the derivative term in integral I_3 we obtain:

$$I_3 = -\sum_{m=0}^{n-1} \int_0^{\infty} e^{-\xi} \xi^s L_n^s(\xi) L_m^s(\xi) d\xi \,. \tag{4.56}$$

In the above integral $m \neq n$ because m can go only upto $(n-1)$. Thus the integral vanishes. Now let us see what is the expectation value of momentum observable, after evaluating the three integrals above. Substituting the non-zero values I_1 and I_2 in Eq. 4.50, it is clear that the expectation value of momentum is zero as has been expected.

C. Position expectation values for various potentials

After a thorough discussion about the momentum expectation values for various solvable one-dimensional potentials, it is worth spending some time discussing about the average position of the particle inside the bound states. Among

all the above examples, in each case we had $V(x) = V(-x)$ except the Morse potential as Morse potential is not an example of a symmetric potential: $V(x) \neq V(-x)$.

In deriving the expectation values of momentum for above symmetric cases, we often considered that the integrals of odd functions over the symmetric limits vanishes. This result does not hold true for the asymmetric Morse potential. Already we have shown that the momentum expectation value: $< p >= 0$ for all the above potentials. When it comes to the expectation values of position, one can easily see that $< x >= 0$ for symmetric potentials whose centers are at the origin. On the other hand if this is not the case, suppose the infinite square well is defined in the range $0 \leq x \leq L$ also then the expectation value of position does not vanish. It becomes $L/2$. Thus, more accurately the average position of the particle is dependent on the symmetry of the potential where as the average momentum is solely guided by the reality of it's eigenvalues and consequently it is zero always.

Below we will briefly discuss how the asymmetry of the potential affects the expectation value of x in the case of the Morse potential. The expectation value of the position operator is:

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} u_n^{\lambda *}(\xi)\, x\, u_n^{\lambda}(\xi) dx. \tag{4.57}$$

The eigen function and the variables are respectively substituted from Eq. (4.44) and Eq. (4.45). We obtain

$$\langle \hat{x} \rangle = \frac{N^2}{\beta^2} \left[\ln(2\lambda) \int_0^{\infty} e^{-\xi} \xi^{s-1} (L_n^s(\xi))^2 d\xi + \int_0^{\infty} e^{-\xi} \xi^{s-1} (L_n^s(\xi))^2 \ln(\xi) d\xi \right]. \tag{4.58}$$

The first integral is already been obtained in Eq. (4.53). This result is independent of the quantum number n. The second integral (say I) is not that straight forward, because it contains associated Laguerre polynomial, logarithm, exponential and monomial functions. Here at best we can evaluate the integral atleast for some specific n as, $n = 0$ or $n = 1$, when the Laguerre polynomial is respectively replaced by 1 and $(-\xi + s + 1)$. For the ground state wave function ($n = 0$), I would be

$$I_{n=0} = \int_0^{\infty} e^{-\xi} \xi^{s-1} \ln(\xi) d\xi, \tag{4.59}$$

which can be written in terms of $\Psi(s)$ and Γ function [18]:

$$I_{n=0} = \Gamma(s)\Psi(s), \tag{4.60}$$

where, $\Psi(s)$ is the logarithmic factorial function, defined as $\frac{d(\ln(s)!}{ds} = \frac{(s!)'}{s!} = \Psi(s)$. For $n = 0$, first integral reduces to $\Gamma(s)$ from Eq. (4.53). Above two evaluations gives the ground state expectation value:

$$\langle \hat{x} \rangle_{n=0} = \frac{1}{r_0 \beta} \left[\ln(s+1) - \Psi(s) \right]. \tag{4.61}$$

For $n = 1$, one can proceed in the same way

$$\begin{aligned} \langle \hat{x} \rangle_{n=1} &= \frac{N^2}{\beta^2} \left[\int_0^{\infty} e^{-\xi} \xi^{s+1} \ln(\xi) d\xi + (s+1)^2 \int_0^{\infty} e^{-\xi} \xi^{s-1} \ln(\xi) d\xi 2(s+1) \int_0^{\infty} e^{-\xi} \xi^{s} \ln(\xi) d\xi \right] \\ &= \frac{N^2}{\beta^2} \left[\Gamma(s+2)\Psi(s+2) + (s+1)^2 \Gamma(s)\Psi(s) - 2(s+1)\Gamma(s+1)\Psi(s+1) \right], \end{aligned} \tag{4.62}$$

which simplifies to give the expectation value corresponding to the second eigen state:

$$\langle \hat{x} \rangle_{n=1} = \frac{1}{r_0 \beta} \left[\ln(s+3) - \Psi(s+2) + \frac{3}{(s+2)}) \right]. \tag{4.63}$$

Other expectation values for $n > 1$ can also be obtained in a similar fashion.

The important point which is to be noted here is, though the average momentum vanishes, the average position is non-zero for Morse potential and remain so, irrespective of the choice of coordinate origin. This result is also true for all eigen states of the same Hamiltonian.

D. Momentum expectation value for a three-dimensional slowly varying spherically symmetric potential

In three dimensions, for a spherically symmetric potential the solution of the Schrödinger equation is given in Eq. (3.4). Here we have assumed that the variables can be separated. The expectation values of $\hat{L}_\theta$ and $\hat{L}_\phi$ have been evaluated in section III. In this section we take the case of the Hydrogen atom and calculate the expectation value of the radial component of the linear momentum.

1. The Hydrogen atom

In this case,

$$V(\hat{r}) = -\frac{e^2}{\hat{r}}\,. \tag{4.64}$$

where e is the electronic charge and $r = \sqrt{x^2+y^2+z^2}$. Now we have to write Eq. (3.2) in spherical polar coordinates and the solution of the time-independent Schrödinger equation is:

$$\begin{aligned} u_{n\,L\,M}(r,\theta,\phi) &= N_r\, R_{n\,L}(r)\, Y_{L\,M}(\theta,\phi)\,, \\ &= N_r\, e^{-r/na_0} \left[\frac{2r}{na_0}\right]^L \mathcal{L}^{2L+1}_{n-L-1}\left(\frac{2r}{na_0}\right) Y_{L\,M}(\theta,\phi)\,, \end{aligned} \tag{4.65}$$

where $a_0 = \frac{\hbar^2}{me^2}$ is the Bohr radius and m is the reduced mass of the system comprising of the proton and the electron. n is the principal quantum number which is a positive integer, $\mathcal{L}^{2L+1}_{n-L-1}(x)$ are the associated Laguerre polynomials, $Y_{L\,M}(\theta,\phi)$ are the spherical-harmonics, and N_r is the normalization arising from the radial part of the eigenfunction. The values which L and M can take is discussed in section III. The radial normalization constant is given by:

$$N_r = \left[\left(\frac{2}{na_0}\right)^3 \frac{(n-L-1)!}{(n+L)!2n}\right]^{1/2}. \tag{4.66}$$

The spherical-harmonics are given by,

$$Y_{L\,M}(\theta,\phi) = \left[\frac{2\,L+1}{4\pi}\frac{(L-M)!}{(L+M)!}\right]^{1/2} P^L_M(\cos\theta) e^{iM\phi}\,, \tag{4.67}$$

where $P^M_L(\cos\theta)$ are the associated Legendre functions. It is noted that although the Coulomb potential is a real potential but the solution in spherical polar coordinates is not real, $e^{iM\phi}$, is complex. The spherical-harmonics are ortho-normalized according to the relation,

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} d\theta\, d\phi\, \sin\theta\, Y_{L\,M}(\theta,\phi) Y_{\tilde{L}\,\tilde{M}}(\theta,\phi) \;= \delta_{L\tilde{L}}\,\delta_{M\tilde{M}}. \tag{4.68}$$

Let us write the eigenfunctions in terms of dimensionless quantity: $\rho = 2r/na_0 \equiv \alpha r$. Also we define $k \equiv (2L+1)$ and $n_r \equiv (n-L-1)$ for the sake of convenience. With this amount of notational machinery the eigenfunctions can be written as:

$$u_{n\,L\,M}(r,\theta,\phi) = N_r\, R_{nL}(\rho)\, Y_{L\,M}(\theta,\phi)\,. \tag{4.69}$$

The radial momentum expectation value in this case is not given by $-i\hbar\langle\frac{\partial}{\partial\rho}\rangle$, its form is (already discussed in section III):

$$\langle\hat{p}_\rho\rangle = -i\hbar\tilde{N}^2 \int_0^\infty d\rho\, \rho^2 R^*_{nL}(\rho)\left[\frac{\partial}{\partial\rho}+\frac{1}{\rho}\right] R_{nL}(\rho)\int d\Omega\,[Y_{L\,M}(\theta,\phi)]^2\,. \tag{4.70}$$

Where $\tilde{N}^2 = N_r^2/\alpha^2$. The integral for the spherical harmonics yields identity. The radial expectation value then becomes,

$$\langle\hat{p}_\rho\rangle = -i\hbar\tilde{N}^2 \int_0^\infty d\rho \left\{-\frac{1}{2}e^{-\rho}\rho^{k+1}[\mathcal{L}^k_{n_r}(\rho)]^2 + (L+1)\,e^{-\rho}\rho^k[\mathcal{L}^k_{n_r}(\rho)]^2 + e^{-\rho}\rho^{k+1}\mathcal{L}^k_{n_r}(\rho)\frac{d}{d\rho}[\mathcal{L}^k_{n_r}(\rho)]\right\}. \tag{4.71}$$

Using the recurrence relation [16]:

$$\frac{d}{d\rho}\mathcal{L}^k_{n_r}(\rho) = \rho^{-1}\left[n_r\,\mathcal{L}^k_{n_r}(\rho) - (n_r+k)\,\mathcal{L}^k_{n_r-1}(\rho)\right], \tag{4.72}$$

the expectation value integral acquires the form:

$$\langle\hat{p}_\rho\rangle = -i\hbar\tilde{N}^2 \int_0^\infty d\rho \left\{-\frac{1}{2}e^{-\rho}\rho^{k+1}[\mathcal{L}^k_{n_r}(\rho)]^2 + (n_r+L+1)\,e^{-\rho}\rho^k[\mathcal{L}^k_{n_r}(\rho)]^2 + e^{-\rho}\rho^k\mathcal{L}^k_{n_r}(\rho)\mathcal{L}^k_{n_r-1}(\rho)\right\}. \tag{4.73}$$

The third contribution of the becomes zero from the orthogonality property of the associated Laguerre polynomials as given in Eq. (4.51). The contribution from the second term can also be found similarly. To find the share of the first term we make use of [19]:

$$\int_0^\infty d\rho\, e^{-\rho}\, \rho^{k+1}\, [\mathcal{L}_{n_r}^k(\rho)]^2 = \frac{(n_r+k)!}{n_r!}\,(2n_r+k+1). \tag{4.74}$$

Collecting all the contributions we get the radial expectation value to be zero as expected.

V. A DISCUSSION ON HEISENBERG'S EQUATION OF MOTION AND EHRENFEST THEOREM

The time evolution of any operator $\hat{O}$ in the Heisenberg picture is given by:

$$\frac{d\hat{O}}{dt} = \frac{1}{i\hbar}[\hat{O}, \hat{H}]\,, \tag{5.1}$$

where $\hat{H}$ is the Hamiltonian of the system. The Hamiltonian of a quantum system comprising of a particle of mass m is given by:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}})\,. \tag{5.2}$$

From the above two equations we can write the time evolution of the momentum operator in one dimension, in Cartesian coordinates as:

$$\frac{d\hat{p}_x}{dt} = \frac{1}{i\hbar}[\hat{p}_x, \hat{H}] = -\frac{d}{dx}V(\hat{x})\,, \tag{5.3}$$

which is the operator version of Newton's second law in a time independent potential. Now if we take the expectation values of both sides of Eq. (5.3) in any basis we get:

$$\frac{d\langle\hat{p}_x\rangle}{dt} = -\left\langle \frac{d}{dx}V(\hat{x})\right\rangle\,, \tag{5.4}$$

and historically the above equation is called the Ehrenfest theorem, which was deduced in a different way by P. Ehrenfest. Using the Ehrenfest theorem we can deduce that the rate of change of the expectation value of the momentum operator is zero in the case of the linear harmonic oscillator. In the case of the linear harmonic oscillator we have:

$$\frac{d}{dx}V(\hat{x}) = m\omega^2\hat{x}\,, \tag{5.5}$$

and it can be trivially shown that $\langle\hat{x}\rangle = 0$. This directly implies that,

$$\frac{d\langle\hat{p}_x\rangle}{dt} = 0\,, \tag{5.6}$$

for the linear harmonic oscillator. The above equation shows that the expectation value of the momentum along x direction is constant, and this constant is zero is known from other sources.

Next we focus on the Hydrogen atom. The Hamiltonian of the Hydrogen atom is:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}\,r + \frac{1}{2mr^2}\hat{\mathbf{L}}^2 - \frac{e^2}{r}\,, \tag{5.7}$$

where,

$$\hat{\mathbf{L}}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\,, \tag{5.8}$$

whose eigenvalues are of the form $\hbar^2 L(L+1)$ in the basis $Y_{L\,M}(\theta,\phi)$. In the expression of the Hamiltonian m is the reduced mass of the system comprising of the proton and electron. Next we try to apply Heisenberg's equation to the

radial momentum operator. Noting that the first term of the Hamiltonian is nothing but $\hat{p}_r^2$ the Heisenberg equation is:

$$\begin{aligned}\frac{d\hat{p}_r}{dt} &= -\frac{\hat{\mathbf{L}}^2}{2m}\left[\frac{1}{r}\frac{\partial}{\partial r}\,r\,,\,\frac{1}{r^2}\right] + e^2\left[\frac{1}{r}\frac{\partial}{\partial r}\,r\,,\,\frac{1}{r}\right]\,,\\ &= \frac{\hat{\mathbf{L}}^2}{mr^3} - \frac{e^2}{r^2}\,. \end{aligned} \tag{5.9}$$

The above equation is the operator form of Newton's second law in spherical polar coordinates. Next we evaluate the expectation value of both the sides of the above equation using the wave-functions given in Eq. (4.65). We know,

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{n^3\, a_0^2 (L+\frac{1}{2})}\,, \tag{5.10}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0^3\, n^3 L(L+\frac{1}{2})(L+1)}\,. \tag{5.11}$$

Using the above expectation values in Eq. (5.9) and noting that $\langle \hat{\mathbf{L}}^2 \rangle = \hbar^2 L(L+1)$ we see that the time derivative of the expectation value of the radial momentum operator of the Hydrogen atom vanishes.

The above analysis shows that the form of the Ehrenfest theorem as given in Eq. (5.4) is only valid in Cartesian coordinates. In the case of the Hydrogen atom if we used Eq. (5.4) we should have never got the correct result.

VI. CONCLUSION

In the present work we have emphasized on the reality of the momentum expectation value and using the reality of the expectation value as a bench mark we did find out the form of the momentum operator in spherical polar coordinate system. We found that most of the concepts which define the momentum operator in Cartesian coordinates do not hold good in spherical polar coordinates and in general in any other coordinate system. The reason being that whenever we do an integration in curvilinear coordinates the Jacobian of the coordinate transformation matrix comes inside the picture and the Cartesian results start to falter if we do not change the rules appropriately. The forms of the momentum along the radial direction and the form of the angular momentum operators are derived in section III. The status of the angular variables was briefly discussed in the same section. We explicitly calculated the expectation values of the momentum operator in various important cases and showed that the expectation value of the momentum operator do really come out to be zero as expected. Although the expectation value of the momentum operator vanishes in most of the bound states, with a real potential, the expectation value of the position is not required to vanish. The expectation value of the position operator is directly related with the parity property of the potential which was briefly discussed in subsection IV C. At the end we calculated the Heisenberg equation of motion for the radial momentum operator for the Hydrogen atom and showed its formal semblance with Newton's second law. It was also shown that if we properly write the Heisenberg equation of motion in spherical polar coordinates then Ehrenfest's theorem follows naturally.

In short we conclude by saying:

1. the forms of the various momentum operators, in most of the coordinate systems, in quantum mechanics can be obtained by imposing the condition of the reality of their eigenvalues. The form of the probability conservation equation and Ehrenfest theorem must be modified in curvilinear coordinates to yield meaningful results.

2. There are obvious problems in elevating the status of angular variables to dynamical variables in quantum mechanics.

3. For compact variables, if the variable is periodic the expectation value of the angular momentum conjugate to it is non-zero. If the compact variable is not periodic then the angular momentum conjugate to it must vanish.

4. The momentum expectation values in cases of bound state motions vanish, whereas the position expectation values in those cases depends on the symmetry of the potential.

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[19] The specific integration result and other related expressions can be found in the web page: http://mathworld.wolfram.com/LaguerrePolynomial.html, Equation 24.